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# PAPER

# Broadening the absorption of conjugated polymers by "click" functionalization with phthalocyanines

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Conjugated copolymer derivatives of poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) and poly(3-hexylthiophene) (P3HT) containing 10% of alkyne functionalities in the side chains have been prepared using the sulfinyl precursor route and the Rieke method, respectively. With the aim of expanding the absorption range of these conjugated polymers for their use in bulk heterojunction (BHJ) polymer:fullerene solar cells, appropriate phthalocyanine (Pc) molecules have been covalently bound through a post-polymerization "click chemistry" reaction between the alkyne functionalities in the side chains of the copolymers and a Pc functionalized with an azide moiety. The resulting poly(*p*-phenylenevinylene)-Pc (**PPV-Pc**) material holds a 9 mol% content of Pcs, while the polythiophene-Pc material (**PT-Pc**) contains a 8 mol% of Pc-functionalization in the side chains. As expected, the presence of the Pc contributes to the extension of the absorption up to 700 nm. BHJ solar cells have been prepared using **PPV-Pc** and **PT-Pc** materials in combination with PCBM. Although the Pc absorption contributes to the generation of photocurrent, the overall power conversion efficiencies (PCE) obtained from these cells are lower than those obtained with BHJ P3HT:PCBM (1:1) and MDMO-PPV:PCBM (1:4) solar cells. A plausible explanation could be the moderate solubility of the **PPV-Pc** and **PT-Pc** materials that limits the processing into thin films.

# Introduction

Polymer:fullerene bulk heterojunction (BHJ) solar cells are promising candidates as sources of renewable energy.<sup>1-3</sup> A continuous improvement on the optoelectronic properties of the active materials and device processing has led to solar cells with efficiencies over 7% today.<sup>4,5</sup> Increasing the efficiency and lifetime of the devices is a challenge that has to be met for potential successful commercialization of this type of solar cell.<sup>1</sup> Often cited examples of polymer:fullerene BHJ solar cells are those containing semiconducting poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) or poly(3-hexylthiophene) (P3HT) as electron donors, and phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM) as the electron acceptor component in the active layer.

Several chemical strategies have been applied to increase the efficiency in BHJ devices. For example, the open circuit voltage  $(V_{\infty})$  and short-circuit current density  $(J_{sc})$  may be improved by a fine-tuning of the donor and acceptor energy levels. In this regard, one of the limitations of conventional P3HT and MDMO-PPV polymers is their narrow absorption window: only light with enough energy for electrons to cross the polymer band gap can be absorbed, that is, only a fraction of what is emitted by the sun. The solar emission spectrum ranges from the UV to the infrared, with a maximum flux around 700 nm. In this regard, extending the absorption of the polymeric material would, in principle, enhance the absorption of the active layer in the device, thus leading to higher short-circuit currents and efficiencies. In this regard, the so-called low band gap polymers<sup>6,7</sup> are candidates for better overlap with the solar spectrum.

Here, we aim to broaden the absorption window of the polymer material following a different approach, *i.e.* through the covalent attachment to the side chains of the polymer backbone of a dye molecule that absorbs longer wavelengths compared to the conjugated polymer. Phthalocyanines (Pcs) are thermally and chemically stable 18- $\pi$  aromatic molecules showing an intense absorption in the red/near infrared (IR) region of the solar spectrum

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(i.e. around 700 nm) with high extinction coefficients and fluorescence quantum yields, which makes them ideal chromophores to enhance the spectral coverage.<sup>8</sup> In addition, Pcs are good ptype semiconductors and present rich redox chemistry, which can be modulated as a function of the peripheral substitution and/or the central metal included in the aromatic cavity. Therefore, once photoexcited, Pcs are capable of acting either as electrondonors when they are connected to appropriate electron-acceptor moieties such as fullerene derivatives,<sup>8-10</sup> or as electron-acceptors when linked to donor systems such as polythiophenes.<sup>11</sup> All these features render Pcs valuable photoactive materials for their incorporation in planar heterojunction<sup>10,12</sup> or bulk heterojunction solar cells13 with fullerenes, as well as in dye sensitized solar cells.14,15 As far as MDMO-PPV and P3HT absorb light with wavelengths ranging from 400 to 600 nm, the incorporation of Pc molecules absorbing from 600 to 700 nm to the active layer will cause a broadening of the absorption range.<sup>16-18</sup> Recently, photoconversion properties extended more than 150 nm toward longer wavelengths have been demonstrated on a P3HT/PCBM blend mixed with a peripherally substituted octabutoxy H<sub>2</sub>Pc, as compared to a device without such Pc-sensitization.<sup>17</sup> Maximum internal quantum efficiencies of ca. 40% were observed in the main absorption region of the Pc (i.e. around 700 nm) for a 10:10:1 ratio of P3HT, PCBM and H<sub>2</sub>Pc, respectively. Another recent work by H. Ohkita and coworkers reports a power conversion efficiency (PCE) of 2.7% of annealed, spin-coated BHJ devices containing a 10:10:1 ratio of P3HT, PCBM and a silicon(IV) Pc derivative, a 20% larger value than the corresponding control device without Pc-sensitization (i.e. 2.2%).<sup>18</sup> The key issue of this result is that the Si(IV)Pc derivative holds axially-linked, branched hydrocarbon chains, which avoid the formation of Pc-aggregates and therefore, permit the allocation of the Si(IV)Pc molecules at the donor (P3HT)/acceptor (PCBM) interface. External quantum efficiency (EQE) measurements indicate that the Si(IV)Pc molecules can contribute to the photocurrent generation by either direct photoexcitation or as energy funnels for P3HT excitons at the P3HT/PCBM interface.

In view of these results, we envision the covalent attachment of Pc molecules at the side chains of P3HT and MDMO-PPV conjugated copolymers, in a proper molar ratio (*i.e.* around a 10% content), as a plausible route to obtain higher photocurrents and increased PCE in BHJ devices of these materials with PCBM. An appropriate content of Pc molecules may lead to enhanced photocurrent generation by photoexcitation of the Pcs; in addition, the covalent binding of the Pcs to the polymer may avoid the aggregation phenomena and enforce the Pcs to interact with both the main chain of the semiconducting polymer and the acceptor PCBM, thus allowing energy transfer from the polymer to the Pc molecules and subsequent electron transfer from the photoexcited Pc to PCBM.

To prepare these polythiophene-Pc (**PT-Pc**, Scheme 1) and poly-*p*-phenylenevinylene-Pc (**PV-Pc**, Scheme 1) materials, a postpolymerization procedure seems to be the most convenient approach. One of the most reliable ways to perform this functionalization is the well-known 1,3 Huisgen cycloaddition between an azide and an alkyne functionality.<sup>19</sup> This "click chemistry" reaction proceeds with very high yields and has been largely applied to the side-chain functionalization of polymers,<sup>20</sup> and also exploited with success for the derivatization of materials, for example carbon nanotubes, with Pcs.<sup>21</sup> Therefore, PPV and P3HTbased alkynyl-terminated copolymers have to be prepared, and further reacted with an unsymmetrically substituted Pc containing solubilizing groups and one azide functionality. Following this approach, a high degree of incorporation of Pc molecules to the functionalized side-chains of the copolymer can be achieved. Reasonable precursors of the alkynyl-terminated PPV and P3HTbased copolymers are the corresponding materials holding lateral chains with ester groups, which can be easily prepared following reported procedures.<sup>22,23</sup>

Therefore, we have synthesized PPV and PT copolymers with approximately 10% content of ester-functionalized alkyl side chains. Basic hydrolysis of the ester and subsequent reaction with propargyl alcohol leads to the corresponding alkynyl-terminated materials, which can further react with azido-containing Pc molecules to give **PT-Pc** and **PPV-Pc** coupled materials with a broader absorption range compared to P3HT or MDMO-PPV. The photovoltaic performance of these materials has been studied in polymer:PCBM BHJ solar cells with several ratios of PCBM.

#### **Results and discussion**

#### Synthesis and characterization

The synthesis of PPVs has been reported by several routes.<sup>22,24,25</sup> In this particular case, the copolymerization reaction of the MDMO monomer 1 and an ester-containing monomer 2 was done using the sulfinyl precursor route (Scheme 1a), yielding the non-conjugated derivative **PPV-1**.<sup>22</sup> Although both monomers are a mixture of regioisomers, for the sake of simplicity only one isomer is depicted in Scheme 1a. Post-polymerization treatment of **PPV-1** with toluene and potassium *tert*-butoxide transformed the ester functionality in the side chains of the conjugated copolymer to a carboxylic acid (**PPV-2**), which was further reacted with propargylic alcohol to give **PPV-3**. This copolymer contains 9% of triple bonds, as determined by <sup>1</sup>H-NMR. A detailed report on the synthesis of these and other alkyne-functionalized PPVs will be published elsewhere.<sup>26</sup>

The synthesis of poly(3-alkylthiophenes) has been achieved using various synthetic routes.27,28 The synthesis of the estercontaining copolymer PT-1, displayed in Scheme 1b, was carried out using the previously reported Rieke method,<sup>23,29</sup> which yields copolymers having a regio-regularity of ca. 90%. After copolymerization of thiophenes 3 and 4 to give PT-1, the ester functionalities in the alkyl side chains were converted to the corresponding acid functions in a 2 M NaOH solution in EtOH. The conversion of the ester-functionalized copolymer PT-1 to the acid-functionalized copolymer PT-2 was complete after stirring for 48 h under reflux. The full conversion was evidenced in <sup>1</sup>H-NMR by the disappearance of the signal originating from the O-CH<sub>2</sub> methylene protons in the ester functionality. Additional proof is the shift of the C=O absorption in FT-IR from 1740 cm<sup>-1</sup> to 1710 cm<sup>-1</sup>. The acid functional groups were reacted in a second step with propargyl alcohol using the DCC/DMAP protocol to give PT- $3.^{30}$  The presence of the triple bond at the end of the alkyl side chains was confirmed in <sup>1</sup>H-NMR by the signal originating from the O–C $H_2$ -C=CH methylene protons in the ester moiety; and the presence of the acetylene proton is visible at  $\delta = 2.42$  ppm. The



Scheme 1 Synthesis of alkyne-containing (a) MDMO-PPV-type copolymer PPV-3 and (b) P3HT-based copolymer PT-3; (c) synthesis of azido-functionalized phthalocyanine Pc-3.

C=O stretch on FT-IR shifts from 1710 cm<sup>-1</sup> in the acid group to 1740 cm<sup>-1</sup> in the ester group. The percentage of functionalized side chains in this copolymer was calculated by integration of the <sup>1</sup>H-NMR signals from the O-CH<sub>2</sub> (4.7 ppm) of the esterfunctionalized side chains and CH<sub>3</sub> groups (0.89 ppm) of the hexyl side chains. The relative ratios indicate that copolymer **PT-3** contains 8% alkynyl moieties.

The synthesis of the azido-phthalocyanine **Pc-3** is depicted in Scheme 1c. First, the statistical cyclotetramerization reaction of 4-*tert*-butylphthalonitrile and 4-(4-hydroxymethylphenyl)phthalonitrile<sup>31</sup> in a 3 : 1 ratio in the presence of Zn(OAc)<sub>2</sub> afforded the Zn(II)Pc precursor **Pc-1**. Bromination of this Pc using CBr<sub>4</sub> gave **Pc-2**, which was converted to the azide derivative **Pc-3** by reaction with an excess sodium azide. <sup>1</sup>H-NMR spectra of these compounds confirms the successful transformation of the OHmoiety into the bromo and azide functionalities through the chemical shift of the adjacent methylene signal (from 4.75, to 4.99 and 4.61, respectively). The azido-containing **Pc-3** shows the typical  $N_3$  stretching band in FT-IR at 2093 cm<sup>-1</sup>. The UV-vis spectrum of this macrocycle exhibits a B band at 350 nm and a single Q band with a maximum at 675 nm.

The reaction conditions for the polymer-Pc coupling *via* "click chemistry" (Scheme 2) were adapted from literature procedures.<sup>32</sup> In order to maximize the number of Pc molecules incorporated to the polymer, different Cu(1) salts, N-ligands and Pc ratios were tested. Finally, the use of 2 equivalents of



Scheme 2 Schematic representation of the "click" reaction of copolymers PPV-3 and PT-3 with Pc-3 to obtain PPV-Pc and PT-Pc, respectively.

**Pc-3** (with respect to the number of acetylene moieties present in the copolymers), CuBr (0.1 eq) and N,N,N',N',N'',N''', pentamethyldiethylenetriamine (PMDETA) (0.1 eq) were found to be optimum conditions for our proposed reaction. Thus, the corresponding polymer (i.e. PPV-3 or PT-3) and 2 eq. of Pc-3 were dissolved in degassed THF, and then CuBr and PMDETA were added under nitrogen flow. After work up and purification, the reaction mixture was spotted on a TLC plate and eluted in a THF-hexane (1:2) mixture. Since the resulting polymer materials **PPV-Pc** and **PT-Pc** do not elute on the TLC plate, the visible spots with retention factor  $(R_f) > 0$  are due to the smaller molecules present in the reaction mixture. Bright blue Pc spots were visible for both experiments before purification. After work up and purification by rinsing with acetone, no blue spots were visible in TLC, a positive verification of removal of all non-reacted Pc molecules. UV-Vis spectroscopy measurements in solution of PPV-Pc and PT-Pc displayed the polymer absorption with a maximum around 450 nm for the PT-containing material, and a maximum at 500 nm for the PPV one, and, in both cases, the absorption at 675 nm of the covalently bound Pc (Fig. 1). The proof that conversion of the  $C \equiv C$  bonds towards the 1.4disubstituted-1,2,3-triazole moiety was fully achieved is provided by the <sup>1</sup>H-NMR spectrum of **PT-Pc** and **PPV-Pc**. The signal of the methylene protons next to the alkyne function at  $\delta = 4.7$  ppm completely disappears, indicating that all present alkyne moieties have reacted with a Pc molecule. Instead, new resonances of the two different methylene moieties close to the triazole are visible in the range of  $\delta = 5.0-5.7$  ppm. In both materials, signals originating from the incorporated Pc units are visible in the aromatic region



**Fig. 1** UV-Vis absorption of (a) a solution of **PPV-Pc** in THF (squares) and in CB (triangles); (b) a film of **PPV-3** drop-cast from a solution in THF (squares) and films of **PPV-Pc** drop-cast from solution in CB (triangles) or THF (circles); (c) **PT-Pc** in solutions of CB (triangles) and THF (black line); (d) films drop-cast from a solution in CB (P3HT: squares, and **PT-Pc**: triangles) and drop-cast from a solution in THF (**PT-Pc**: circles).

between  $\delta = 7.5$  and 8 ppm, together with the signal of the triazole ring.

#### UV-Vis spectroscopy measurements

The UV-Vis absorption spectra of PPV-Pc solutions in THF and chlorobenzene (CB) are displayed in Fig. 1a. The absorption between 400 and 550 nm with wavelength of maximum absorption  $(\lambda_{max})$  around 510 nm is due to the conjugated backbone of the PPV, while the absorptions at ca. 350 nm and between 650 and 700 nm is due, respectively, to the Soret and O band absorptions of the Pc molecules covalently bound to the side chains. In THF and CB, the  $\lambda_{max}$  of the Q band is at 676 nm and 691 nm, respectively. Red-sifting of the O band in solutions of Pcs in aromatic solvents has been previously observed and rationalized in terms of stabilization of the LUMO level of the Pc through coordination of the aromatic solvent. In fact, precursor azidophthalocyanine **Pc-3** shows a  $\lambda_{max}$  of its Q band in CB at 684 nm, whereas this Pc exhibits a  $\lambda_{max}$  at 675 in THF solution. A solventinduced interaction between the Pc moiety and the conjugated PPV backbone can explain the additional red-shifting observed in CB solution of PPV-Pc with regard to that of Pc-3.

In Fig. 1b, the UV-Vis spectra of alkyne-functionalized **PPV-3** and **PPV-Pc** in film are given. The absorption of **PPV-3** is comparable to the absorption of **MDMO-PPV** between 400 and 550 nm with  $\lambda_{max}$  at 512 nm. In the **PPV-Pc** film, the Pc absorption is visible with  $\lambda_{max}$  at 692 nm, while the  $\lambda_{max}$  of the PPV decreases to 494 nm. The shift to lower wavelengths of the PPV absorption in **PPV-Pc** as compared to **PPV-3** indicates that the presence of the Pc in the side chains disturbs the polymer organization and lowers effective conjugation length. The  $\lambda_{max}$  of the Pc Q band in the **PPV-Pc** film almost coincides with that obtained in CB solution, this fact being an indication of the interaction between the conjugated PPV backbone and the Pc molecules, which produces a stabilization of the LUMO level of the Pc as in the case of dilution in aromatic solvents.

The absorption spectra of PT-Pc solutions in THF and CB are displayed in Fig. 1c. The PT absorption has a  $\lambda_{max}$  around 450 nm. The contribution of the Pc in the absorption is visible at ca. 350 nm, and between 600 and 700 nm, with  $\lambda_{max}$  around 675 nm. In THF solution, the Pc absorption appears at  $\lambda_{max}$  677 nm, while in CB solution the  $\lambda_{max}$  of the Pc was at 691 nm for **PT-Pc**. The UV-Vis spectra of PT-Pc films drop-cast from solutions in CB and THF are displayed in Fig. 1d, together with the absorption of regio-regular P3HT in CB. Although the spectra are affected by scattering, they show that, compared to the absorption in solution, the absorption of the polymer backbone in PT-Pc broadens relative to the Q band of the Pc component, as a consequence of the  $\pi$ - $\pi$  stacking of the conjugated chains of the PT part. The PT absorption is also red-shifted compared to the spectrum in solution, with maximum absorptions at 523 nm for the film drop-cast from CB and 564 nm for the film drop-cast from THF, respectively. The absorption at 600 nm in both THF- and CB-drop-casted films is due to the ordering of regio-regular PT chains.<sup>33</sup> The contribution of the absorption in the visible of the Pc moiety was found at around 690 nm. The higher  $\lambda_{max}$ , together with the higher relative intensity of the shoulder at 600 nm of the polymeric backbone in the film drop-cast from THF compared to the corresponding values of the film drop-cast from CB, seem to indicate that the former presents

a better stacking of the PT chains.<sup>34</sup> Therefore, THF seems to be a better solvent than CB to induce a better organization of the polymer chains in the film: THF appears to minimize the impact of the large Pc molecules in the alkyl side chains on the structural ordering of the polymer chains.

#### Cyclic voltammetry

Electrochemical data (V vs. Fc/Fc<sup>+</sup>) of the redox process of Pc-2, which was used as reference compound, were obtained from cyclic voltammetry. The measured potentials in o-DCB solution (1 mol dm<sup>-3</sup> TBAPF<sub>6</sub>) of the onsets of the redox waves for Pc-2 were:  $E_{\rm red}^{1} = -1.373$  V,  $E_{\rm ox}^{1} = 0.005$  V, and  $E_{\rm ox}^{2} = 0.749$  V. The first oxidation and reduction potential are used to estimate the energy of the HOMO and LUMO levels using  $Fc/Fc^{+} = -5.23$ eV with respect to the vacuum level.35 The HOMO and LUMO energy levels of Pc-2 were found to be -5.2 eV and -3.9 eV, respectively. In Fig. 2, the energy levels of Pc-2 are schematically represented in comparison with those determined for MDMO-PPV, P3HT, and PCBM in a similar way. Considering the relative position of the LUMO levels, the Pc molecules could, apart from acting as an absorber, also act as an electron acceptor relative to P3HT and as an electron donor relative to PCBM. The same situation applies to the combination with MDMO-PPV. The fact that the HOMO level of Pc-2 is similar to that of P3HT and MDMO-PPV is advantageous as the Pc molecule in PT-Pc and Pc-PPV will not act as a hole trap. In addition, the small HOMO-HOMO offset will likely result in energy transfer from the PT and PPV polymers to the Pc molecule, followed by electron transfer to PCBM. These events are plausible, since photoexcited charge transfer from the Pc component to C<sub>60</sub> or PCBM has been widely demonstrated in many different device configurations, even in P3HT/PCBM BHJ solar cells containing a 10% of free, unsubstituted Pc chromophore.<sup>17,18</sup> On the other hand, some previous studies performed by us in solution of related, covalent PPV-Pc short oligomers reveal a photosensitization of the Pc units when exciting the PPV chains.<sup>36</sup>



Fig. 2 Energy scheme of the absorbing materials in PT-Pc:PCBM and PPV-Pc:PCBM solar cells.

#### BHJ solar cells fabrication and characterization

**PT-Pc** copolymers were mixed in polymer:PCBM 1:1 and 1:2 (w/w) blends, and **PPV-Pc** in 1:4 blends. Mixed solutions in CB were spin-coated at several spinning speeds to obtain varying



**Fig. 3** EQE of solar cells with (a) **PPV-Pc**:PCBM (1:4) active layer or (b) **PT-Pc** in blends with PCBM in a (1:1) and (1:2) weight ratio; and *J*–*V* curve of ITO/PEDOT:PSS (~50 nm)/polymer:PCBM/LiF/Al devices with (c) **PPV-3**:PCBM (1:4) (squares) and **PPV-Pc**:PCBM (triangles); (d) **PT-1**:PCBM (1:1) (squares) and **PT-Pc**:PCBM (1:2) (triangles).

active layer thicknesses. Therefore, devices with a configuration ITO/PEDOT:PSS/polymer:PCBM/LiF/Al were prepared. As mentioned above, THF seems to be the best solvent to induce structural order of the polymer chains in the film, at least in the case of **PT-Pc**. However, the use of CB is compulsory to dissolve a sufficient amount of PCBM. In CHCl<sub>3</sub> or THF, PCBM could not be dissolved completely and layers spin-coated from solutions of **PT-Pc** or **PPV-Pc** and PCBM in these solvents were rough, and the corresponding devices were of low-efficiency or shunted.

## Photocurrent generation

In the spectral response of BHJ solar cells with a **PPV-Pc**:PCBM (1:4) active layer (Fig. 3a), there is a clear contribution in the EQE of the covalently bound Pc molecules. The contribution of the PPV backbone is visible around 500 nm, and that of the Pc around 700 nm. Comparing the EQE with the UV-Vis absorption spectrum of a **PPV-Pc** film, the absorption peaks of the PPV backbone and the Pc remain at the same wavelength: however, the height of the Pc peak relative to the PPV signal differs. In the spectral response the relative intensity of the Pc Q-band is higher.

Also in the spectral response of **PT-Pc**:PCBM solar cells (Fig. 3b), the EQE due to the Pc component is clearly present around 700 nm, indicating that the light absorbed by the Pc moiety leads to charge transfer, and the generated charges are extracted. The low values of the EQE between 350–550 nm, due to

polythiophene:PCBM also indicates a lack of crystalline ordering of the PT part in spin-coated films as compared to drop cast films (Fig. 1d), which is important for high conversion efficiencies in P3HT:PCBM solar cells.

#### **Device performances**

The best **PPV-3**:PCBM and **PPV-Pc**:PCBM solar cells are displayed in Fig. 3c, and the device parameters of the solar cells of each copolymer are given in Table 1. The performance of devices with **PPV-3** is quite comparable to what is reported for MDMO-PPV:PCBM (1:4) BHJ solar cells.<sup>37</sup> The presence of 10% of alkyne functionalized side chains has little or no effect in the device, and thus, a PCE of 2.2% was achieved. In solar cells with **PPV-Pc**:PCBM (1:4) blends, however, there is a decrease in  $J_{sc}$ ,  $V_{oc}$  and fill factor (FF). The detrimental effect of the Pc molecule on the solubility of the polymer in CB could be largely responsible for the poor device performance, since it causes a poor polymer organization, as was evidenced in the UV-Vis spectrum (see Fig. 1b). This will cause an unfavourable morphology and lower hole mobility in the blend, and consequently, low  $J_{sc}$  and FF. The decrease in  $V_{oc}$  could be due to device defects.

The J-V curves of the best **PT-1**:PCBM and **PT-Pc**:PCBM solar cells are shown in Fig. 3d. The performance of the device **PT-1** as donor component was comparable to the performance of P3HT:PCBM solar cells prepared following the same procedure.<sup>29</sup>

Polymer:PCBM	$J_{ m sc}~({ m mA~cm^{-2}})$	$V_{\rm oc}$ (V)	FF	PCE (%)	Layer thickness (nm)
<b>PT-1</b> (1:1)	5.81	0.65	0.49	1.86	73
<b>PT-Pc</b> (1:2)	1.79	0.67	0.34	0.41	42
<b>PT-Pc</b> (1:1)	1.46	0.68	0.33	0.32	33
<b>PPV-3</b> (1:4)	4.25	0.85	0.62	2.22	80
<b>PPV-Pc</b> (1:4)	3.36	0.66	0.35	0.77	100

The best performing PT-Pc:PCBM solar cells (Table 1) were obtained using a relatively thin layer (42 nm). Better current densities and efficiencies were achieved with higher amounts of PCBM. The low  $J_{sc}$  values of **PT-Pc**:PCBM solar cells compared to P3HT:PCBM solar cells, together with the fact that the best current densities were obtained for very thin layers (thickness < 50 nm), indicated that the charge transport properties in the blend were unfavourable. The low FF of the devices and the need of more PCBM to improve the extraction of charges indicate that also the morphology of the blended layer is poor. Thermal treatment of P3HT:PCBM solar cells has been reported to result in better hole transport in the polymer phase because of closer stacking of the conjugated polymer backbones and a phase separated morphology.<sup>38</sup> However, annealing treatments of the PT-Pc devices did not lead to better results. The Pc molecules in the side chains may prevent the PT chains from self-organizing, this fact explains why no better results are obtained after annealing. A better  $\pi$ - $\pi$  stacking would be obtained by processing from THF, but the solubility of PCBM in this solvent was too low for device preparation. A better solubility in the processing solvent might lead to an enhanced polymer organization in the blend and to an improved morphology, both increasing the PCE.

## Experimental

#### General

The preparation of monomers 2 and 4, the copolymerization reactions to prepare PPV-1 and PT-1 and post-polymerization transformations to give PPV-2 and PPV-3 will be reported elsewhere. <sup>1</sup>H-NMR spectra were recorded on a Varian Inova 300 spectrometer at 300 MHz in a 5 mm probe using deuterated chloroform or tetrahydrofuran, obtained from Cambridge Isotope Laboratories. Chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) using the peak of residual CHCl<sub>3</sub> as an internal standard at  $\delta = 7.24$  ppm in chloroform, or the polythiophene aromatic proton peak at  $\delta = 6.96$  ppm in tetrahydrofuran. Fourier transform infrared spectroscopy (FT-IR) was performed on a Perkin Elmer Spectrum One FT-IR spectrometer using pellets in KBr or films drop-cast on a NaCl disk from solution in chlorobenzene or tetrahydrofuran. Gas chromatography/mass spectrometry (GC-MS) was carried out on TSQ-70 and Voyager mass spectrometers. UV-Vis spectra were recorded on a Varian CARY 500 UV-Vis-NIR spectrophotometer from 200 to 800 nm at a scan rate of 600 nm min<sup>-1</sup>. Size exclusion chromatography (SEC) was performed with a 1 wt% polymer solution in THF, which was filtered with a 0.45 µm pore PTFE syringe filter. A Spectra Physics P100 pump equipped with two

mixed-B columns (10  $\mu$ m, 30 cm  $\times$  7.5 mm) Polymer Labs and a Shodex refractive index detector at 40 °C in THF at a flow rate of 1.0 ml min<sup>-1</sup> were used. Molecular weight distributions were measured relative to polystyrene standards and toluene was used as a flow rate marker.

Electrochemical measurements were performed at room temperature under an inert atmosphere with a scan rate of 0.1 V s<sup>-1</sup>, using 1 M tetrabutylammonium hexafluorophosphate in o-DCB as the electrolyte. The working electrode was a platinum disk and the counter electrode was a silver rod electrode. A silver wire coated with silver chloride (Ag/AgCl) was used as quasi-reference electrode in combination with Fc/Fc<sup>+</sup> as internal standard. The vacuum level of Fc/Fc<sup>+</sup> is assumed at -5.23 eV. Solar cells were made on glass substrates  $(3 \times 3 \text{ cm})$  with patterned ITO electrodes. The substrates were sonicated in acetone, cleaned with soapy water and isopropanol and treated with UV/O<sub>3</sub> for 15 min. Typically, 50 nm poly(ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT: PSS) (Clevios<sup>™</sup> P VP AI 4083, HC Starck) was spin-coated at 3000 rpm. 1.0 wt% and 1.5 wt% solutions of PCBM in chlorobenzene were added to the polymer in (1:1) and (1:2) (w/w) ratios respectively. The solutions were stirred at 50 °C before they were spin-coated at several spinning speeds to investigate the influence of active layer thickness. The preparation of P3HT:PCBM solar cells was with P3HT obtained from Rieke Metals. 1 nm of LiF and 100 nm of Al were evaporated in high vacuum ( $p = 10^{-7}$  mbar). J–V curves were measured under simulated solar light (100 mW cm<sup>-2</sup>) from a tungsten-halogen lamp filtered by a Schott GG385 UV filter and a Hova LB120 daylight filter using a Keithley 2400 source meter. Spectral response was measured with monochromatic light from a 50 W tungsten halogen lamp (Philips focusline) in combination with a monochromator (Oriel, Cornerstone 130) and a lock-in amplifier (Stanford research Systems SR830). A calibrated Si cell was used as reference. The device was kept behind a quartz window in a nitrogen filled container. To measure the cell under appropriate operation conditions, the cell was illuminated by a bias light from a 532 nm solid state laser (Edmund Optics).

## Synthesis of PPV and PT precursors

Poly([2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene]-*co*-[2-methoxy-5-(6-(prop-2-yn-oxy carbonyl)hexyloxy)-1,4phenylenevinylene]) (PPV-3). Copolymer PPV-3 containing 9% of akynyl-terminated side chains was obtained and characterized. Characterization is given to enable interpretation of results. GPC (THF):  $M_w$  = 380 000 g mol<sup>-1</sup>,  $M_w/M_n$  = 5.2;  $\lambda_{max}$ (THF)/nm 507;  $v_{max}/cm^{-1}$  3058, 2954, 2927, 2868, 1745, 1505, 1464, 1414, 1384, 1352, 1258, 1158, 1092, 1037, 969 and 860;  $\delta_H$ (300 MHz; CDCl<sub>3</sub>) 7.6–7.4 (2 H, m, olef. H) 7.2–7.1 (2 H + 2 H<sub>f</sub>, m, arH), 4.65 (2 H<sub>f</sub>, s, OCH<sub>2</sub>), 4.1–3.8 (5 H + 5 H<sub>f</sub>, m, OCH<sub>2</sub>, OCH<sub>3</sub>), 2.4 (2 H<sub>f</sub>, m, CH<sub>2</sub>COO), 2.3 (2H + 2H<sub>f</sub>, m, CH<sub>2</sub>CH<sub>2</sub>O) and 1.8–0.6 (15 H, m, CHC=C, CH, CH<sub>2</sub> and CH<sub>3</sub>).

Poly([3-hexylthiophene-2,5-diyl]-*co*-[3-(6-ethoxycarbonylhexyl)thiophene-2,5-diyl]) (PT-1). Copolymer PT-1 containing 10% of functionalized side chains was obtained and characterized. Characterization is given to enable interpretation of results. GPC (THF):  $M_w = 76~700$  g mol<sup>-1</sup>,  $M_w/M_n = 1.9$ ;  $\lambda_{max}$  (Film)/nm 555 and 602(sh);  $v_{max}/cm^{-1}$  3053, 2954 s, 2925 vs, 2855 s, 1738, 1562, 1509, 1455, 1377, 1261, 1180 1094, 1030, 821 and 725;  $\delta_{\rm H}$ (300 MHz; CDCl<sub>3</sub>) 6.96 (1 H + 1 H<sub>f</sub>, s, Th), 4.10 (2H<sub>f</sub>, c, OCH<sub>2</sub>), 2.79 (2 H, t, α-CH<sub>2</sub>), 2.56 (2 H + 2 H<sub>f</sub>, t, α-CH<sub>2</sub>), 2.31 (2 H<sub>f</sub>, t, CH<sub>2</sub>COOEt), 1.7 (2 H + 2 H<sub>f</sub>, m, β-CH<sub>2</sub>), 1.5–1.2 (6 H + 4H<sub>f</sub>, m, γ, δ, ε-CH<sub>2</sub>) and 0.90 (3 H + 3 H<sub>f</sub>, t, CH<sub>3</sub>).

**Poly([3-hexylthiophene-2,5-diyl]**-*co*-[**3**-(**6**-carboxyhexyl)thiophene-2,5-diyl]) (PT-2). 1.00 g of the 9/1 copolymer PT-1 was stirred for 48 h in 100 ml of a 2 M NaOH solution in EtOH under reflux. The mixture was poured out in a MeOH/2 M HCl mixture and filtrated. The isolated copolymer was dried to obtain 0.95 g (96%) of **PT-2**. GPC (THF):  $M_w = 51\ 000\ \text{g mol}^{-1}$ ,  $M_w/M_n = 1.7$ ;  $v_{\text{max}}/\text{cm}^{-1}$  2954, 2924, 2853, 1710, 1635, 1507, 1457, 1377, 1261, 1077, 820, 803 and 725;  $\delta_{\text{H}}(300\ \text{MHz}; \text{CDCl}_3)$  6.96 (1 H + 1 H<sub>f</sub>, s, Th), 2.79 (2 H, t, α-CH<sub>2</sub>), 2.56 (2 H + 2 H<sub>f</sub>, t, α-CH<sub>2</sub>), 2.37 (2 H<sub>f</sub>, m, CH<sub>2</sub>COOH), 1.7 (2 H + 2 H<sub>f</sub>, m, β-CH<sub>2</sub>), 1.4, 1.3 and 1.2 (6 H + 4 H<sub>f</sub>, m, γ,  $\delta_i \in$ -CH<sub>2</sub>) and 0.90 (3 H, CH<sub>3</sub>).

Poly([3-hexylthiophene-2,5-diyl]-*co*-[3-(6-(prop-2-yn-oxycarbonyl)hexyl)thiophene-2,5-diyl]) (PT-3). 100 mg of the (x/y) 0.90/0.10 acid functionalized polymer PT-2 was dissolved in chlorobenzene before addition of propargylic alcohol (90 mg), DCC (80 mg) and DMAP (4 mg). The reaction was stirred for 48 h at 50 °C. The mixture was precipitated in MeOH, stirred for 1 h and filtrated to obtain 60 mg of the alkyne-functionalized copolymer PT-3 with x/y = 0.92/0.08. GPC (THF):  $M_w = 31\,800$  g mol<sup>-1</sup>,  $M_w/M_n = 1.9$ ;  $v_{max}/cm^{-1}$  3055, 2956 s, 2926 vs, 2855 s, 1746, 1656, 1562, 1509, 1455, 1377, 1261, 1156, 1092, 1021, 820, 801 and 725;  $\delta_{\rm H}(300$  MHz; CDCl<sub>3</sub>) 6.96 (1 H + 1 H<sub>f</sub>, s, Th), 4.65 (2 H<sub>f</sub>, s, OCH<sub>2</sub>), 2.78 (2 H, t, α-CH<sub>2</sub>), 2.54 (2 H + 2 H<sub>f</sub>, t, α-CH<sub>2</sub>), 2.42 (1 H<sub>f</sub>, s, CHC=C), 2.37 (2 H<sub>f</sub>, t, CH<sub>2</sub>COOR), 1.7, 1.4 and 1.3 (8 H + 6 H<sub>f</sub>, m, β, γ,  $\delta_r$ , ε-CH<sub>2</sub>) and 0.89 (3 H, t, CH<sub>3</sub>).

#### Synthesis of phthalocyanine precursors

2,9,16-tri-*tert*-butyl-23-(4'-hydroxymethyl phenyl) Zinc(II) phthalocyaninato(2-)- N29, N30, N31, N32 (Pc-1) (only one regioisomer is named). 4-tert-butylphthalonitrile (709 mg, 3.84 mmol), 4-(4'-hydroxymethylphenyl) phthalonitrile<sup>31</sup> (300 mg, 1.28 mmol) and Zn(OAc)<sub>2</sub> (305 mg, 1.66 mmol) in DMAE (5 mL) were stirred at 110 °C under argon atmosphere for 16 h. After cooling to room temperature, the reaction mixture was treated with MeOH-H<sub>2</sub>O (3:1) (15 mL), and the solid obtained was filtered, washed with MeOH and vacuum-dried. The resulting blue solid was purified by column chromatography on silica gel using hexane/dioxane (2:1) as eluent. The symmetrically tert-butyl substituted phthalocyanine was firstly eluted followed by the unsymmetrically derivative Pc-1. The latter was obtained as a blue solid (250 mg, 25%). Mp > 250 °C;  $\lambda_{max}$ (THF)/nm 675 (log  $\varepsilon$  5.3), 609 (4.5) and 350 (4.8);  $v_{\rm max}/{\rm cm}^{-1}$  2959, 1728, 1607, 1483, 1090, 1047, 831 and 764;  $\delta_{\rm H}$ (300 MHz; DMSO) 9.4–8.9 (8 H, m; Pc-H), 8.4-8.1 (6 H, m, Pc-H and phenyl-H), 7.8-7.7 (2 H, m, phenyl-H), 5.45 (1 H, s, CH<sub>2</sub>OH), 4.75 (2 H, s, CH<sub>2</sub>OH) and 1.81 (27 H, s, C(CH<sub>3</sub>)<sub>3</sub>); m/z (MALDI-TOF) 850-857, C<sub>51</sub>H<sub>46</sub>N<sub>8</sub>OZn (850.31).

Zinc(II) 2,9,16-tri-*tert*-butyl-23-(4'-bromomethyl phenyl) phthalocyaninato(2–)- N29, N30, N31, N32 (Pc-2) (only one regioisomer is named). PPh<sub>3</sub> (197 mg, 0.75 mmol) and CBr<sub>4</sub> (249 mg, 0.75 mmol) were added to a solution of Pc-1 (200 mg, 0.23 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (8 mL) under an argon atmosphere. After stirring at 50 °C for 1 h, the reaction mixture was washed with a saturated aqueous solution of NaHCO<sub>3</sub>, dried over MgSO<sub>4</sub>, and vacuum concentrated. Purification by column chromatography on silica gel with hexane/dioxane (3 : 1) as eluent afforded **Pc-2** as a blue solid (174 mg, 88%). Mp > 250 °C;  $\lambda_{max}$ (THF)/nm 675 (log  $\varepsilon$  5.3), 609 (4.6) and 350 (4.9);  $v_{max}$ /cm<sup>-1</sup> 2959, 1728, 1607, 1483, 1090, 1047, 831 and 764;  $\delta_{\rm H}$ (300 MHz; DMSO) 9.4–8.9 (8 H, m, Pc-H), 8.4–8.1 (6 H, m, Pc-H and phenyl-H), 7.8–7.7 (2 H, m, phenyl-H), 4.99 (2 H, s, CH<sub>2</sub>Br) and 1.80 (27 H, s, C(CH<sub>3</sub>)<sub>3</sub>); *m/z* (MALDI-TOF) 912–919, C<sub>51</sub>H<sub>45</sub>BrN<sub>8</sub>Zn (912.22).

2,9,16-tri-tert-butyl-23-(4'-azidomethyl Zinc(II) phenvl) phthalocyaninato(2-)- N29, N30, N31, N32 (Pc-3) (only one regioisomer is named). Sodium azide (1.21 g, 18.6 mmol) and Pc-2 (0.170 g, 0.186 mmol) were dissolved in DMF-H<sub>2</sub>O (10:1) (22 mL) and heated to 70 °C for 4 h. After cooling down to room temperature, the solvent was removed and the crude was extracted with CH<sub>2</sub>Cl<sub>2</sub> and dried over Na<sub>2</sub>SO<sub>4</sub>. Solvent was evaporated and the resulting solid filtered and washed with hexane to give Pc-3 as a blue solid (0.149 g, 91%). Mp > 250 °C;  $\lambda_{max}$ (THF)/nm 675 (log  $\varepsilon$  5.6), 609 (4.9) and 350(5.2);  $v_{\text{max}}/\text{cm}^{-1}$  2959, 2093 (N<sub>3</sub>), 1728, 1607, 1483, 1090, 1047, 831 and 764;  $\delta_{\rm H}$ (300 MHz; THF) 9.5-9.1 (9 H, m, arom. H), 8.4-8.1 (7 H, m, arom. H), 4.61 (2 H, s, CH<sub>2</sub>N<sub>3</sub>) and 1.84 (27 H, s, C(CH<sub>3</sub>)<sub>3</sub>); m/z (MALDI-TOF) 875-882, C<sub>51</sub>H<sub>45</sub>N<sub>11</sub>Zn (875.32).

#### Synthesis of PPV-Pc and PT-Pc

**General procedure.** Dry THF was degassed by sonicating while an argon flow was sent continuously through the solvent. The polymer was dissolved in THF by stirring at 50 °C, before adding **Pc-3** and other reagents. Equivalents were calculated relative to the number of alkyne functions present in the copolymer. The reactions were stirred in the dark under reflux and inert atmosphere. CuBr (0.1 eq) and PMDETA (0.1 eq.) were added to the polymer with 2 eq. of **Pc-3** in THF (10 mL). The work-up was carried out by filtering the reaction over Al<sub>2</sub>O<sub>3</sub> and washing with THF and CH<sub>2</sub>Cl<sub>2</sub> (**PPV-Pc**) or CHCl<sub>3</sub> (**PT-Pc**). Subsequently, the total volume was reduced to 15 mL by evaporation under reduced pressure and the resulting solution was precipitated dropwise in MeOH. The resulting copolymer was filtered off, washed extensively with MeOH and acetone and dried at room temperature under reduced pressure.

**PPV-Pc. PPV-3** (50 mg) was dissolved before adding **Pc-3** (31 mg, 0.036 mmol), distilled PMDETA (0.3 mg, 0.0017 mmol) and Cu(1)Br (0.3 mg, 0.0020 mmol). After purification, **PPV-Pc** (60 mg) was isolated. GPC (THF):  $M_w = 302\,000\,\text{g}\,\text{mol}^{-1}$ ,  $M_w/M_n = 4.0$ ;  $\lambda_{\text{max}}$ (THF)/nm 352, 509 and 676;  $\lambda_{\text{max}}$ (CB)/nm 358, 510 and 691;  $\lambda_{\text{max}}$ (Thin film)/nm 494 and 692;  $v_{\text{max}}/\text{cm}^{-1}$  3058, 2959, 2927, 2869, 1737, 1504, 1464, 1414, 1385, 1351, 1260, 1205, 1027, 970, 862 and 800;  $\delta_{\text{H}}$ (300 MHz; THF) 9.58–9.38, 8.30, 8.11, 7.90, 7.55–7.4, 7.3–7.1, 5.70, 5.21, 4.1–3.8, 2.4–2.3 and 1.8–0.7.

**PT-Pc. PT-3** (60 mg) was dissolved, and **Pc-3** (61 mg, 0.070 mmol), PMDETA (0.6 mg, 0.0035 mmol) and CuBr (0.5 mg, 0.0035 mmol) were subsequently added. After purification, **PT-Pc** (36 mg) was isolated. GPC (THF):  $I_w = 58\ 600\ \text{g mol}^{-1}$ ,  $M_w/M_n = 1.8$ ;  $\lambda_{\text{max}}$ (THF)/nm 352, 459 and 677;  $\lambda_{\text{max}}$ (CB)/nm 358, 458 and 691;  $\lambda_{\text{max}}$ (Thin film, drop-cast from THF)/nm 564 and 694;  $\lambda_{\text{max}}$ (Thin film, drop-cast from CB)/nm 523 and 692;

 $v_{\text{max}}$ /cm<sup>-1</sup> 2957 s, 2927 vs, 2856 s, 1739, 1644 br, 1511 w, 1487 w, 1456, 1390 w, 1363 w, 1331 w, 1261, 1231 w, 1186 w, 1152 w, 1092, 1048, 1024, 920, 820, 800 and 748;  $\delta_{\text{H}}$ (300 MHz; THF) 8.14, 7.97, 7.76, 7.44, 7.35, 6.96, 6.89 6.83, 6.79, 5.60, 5.06, 2.80, 2.67, 2.40, 2.04, 1.91, 1.77, 1.34, 1.27 and 0.91.

## Conclusions

Conjugated polythiophene- and polyphenylenevinylene-type copolymers decorated with Pc molecules (PT-Pc and PPV-Pc) have been successfully synthesized by post-polymerization "click chemistry" reactions. Copolymers containing ca. 10% alkyne functions in the side chains (i.e. PT-3 and PPV-3) react with an azidofunctionalized Pc molecule (Pc-3) to yield the corresponding Pc-containing polymers PPV-Pc and PT-Pc. Integration of the <sup>1</sup>H-NMR signals of the alkyl side chains indicated that the Pc content in the final copolymers is 8% in the case of PT-Pc, and 9% for the **PPV-Pc** material. These Pc-containing polymers were applied in BHJ solar cells with PCBM in 1:4 blends for PPV-Pc, and 1:1 and 1:2 blends for PT-Pc. The spectral response showed, in both materials, a clear contribution of the Pc around 700 nm to the photocurrent, this fact indicating that the light absorbed by the Pc moiety leads to charge transfer processes, and that the generated charges are collected. Therefore, with this approach we succeeded in broadening the absorption of the active layer in polymer solar cells. However, solubility of the materials in CB (the processing solvent) is not good enough for a correct processing, especially in the case of PT-Pc, and, therefore, the nanoscale organization of the materials in the active layer is not appropriate to achieve efficient devices. Nevertheless, continued efforts in materials design, namely, incorporation of other peripheral substituents to the Pc core to enhance the solubility of the final material and/or changes in the ratio of covalently bound Pcs, can lead to better processed polymer-Pc materials which could lead to more efficient devices.

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